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FORM PTO-1390 (Modified) (REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
7616/21

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR
09/673204

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US99/07970	**12 April 1999**	**13 April 1998**

TITLE OF INVENTION
Modification of Polymer Optoelectronic Properties After Film Transition by Impurity Addition or Removal

APPLICANT(S) FOR DO/EO/US
Sturm, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Small Entity Statement

PCTUS1/REV03

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/673204	PCT/US99/07970	7616/21

21. The following fees are submitted:.

	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1,000.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but Internation Search Report prepared by the EPO or JPO **$860.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**		
☒ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$690.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$130.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	36 - 20 =	16	x $18.00	**$288.00**	
Independent claims	6 - 3 =	3	x $78.00	**$234.00**	
Multiple Dependent Claims **(check if applicable)**.			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS			=	**$1,342.00**	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable)**.			☒	**$671.00**	
SUBTOTAL			=	**$671.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).			+	**$0.00**	
TOTAL NATIONAL FEE			=	**$671.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable)**.			☐	**$0.00**	
TOTAL FEES ENCLOSED			=	**$671.00**	
				Amount to be: refunded	$
				charged	$

☐ A check in the amount of to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **06-2143** in the amount of **$671.00** to cover the above fees. A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **06-2143** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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REGISTRATION NUMBER

10\12\00
DATE

09/673204
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MODIFICATION OF POLYMER OPTOELECTRONIC PROPERTIES AFTER FILM FORMATION IMPURITY ADDITION OR REMOVAL

SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to methods of making semiconductor devices using light emitting organic materials, and more specifically, to methods which involve the modification of the properties of an organic film after it has been deposited by either: (i) adding new components into the film from a top or bottom surface; or (ii) by causing components to leave the film from a top or bottom surface.

RELATED ART

Polymers and blends of polymers and small organic molecules have recently been extensively used to fabricate organic light emitting diodes and thin film transistors.

Organic films are typically deposited in thin film form for electrical and optoelectronic applications by uniformly coating a surface by spin-coating or other methods. Sometimes the final organic film itself is not directly formed, but a precursor is deposited which is converted to a polymer by a subsequent step, such as heating or exposure to UV light (e.g. PPV). It is also well known that adding various elements to the organic film can change its electrical and/or optical properties. These may include elements to change the conduction of electrical carriers (e.g. PBD for electron transportability), or dye centers to change the color of photo- and electro-luminescence (e.g. coumarin 6 in PVK). These extra elements are usually added to the original material before the final solid film is deposited. For example, these different groups could be bonded to a polymer chain before the polymer is deposited by spin coating, or may just be added as other polymers or individual smaller molecules to the solution containing the polymer before a thin film is formed. In either case all materials in the original solution become part of the final film.

The goal of fabricating full color flat panel displays has the potential to be reached using organic light emitting diodes (OLEDs). The difficulty with using this technology is that the current deposition techniques, such as spin-coating and evaporation, deposit blanket films. The film can be used to make devices of a single color. To achieve individual emitters of different color next to each other, such as red, green, and blue, the deposited blanket film must be typically etched into a pattern, as might be done by photolithography followed by etching. Then, this process has to be repeated for multiple layers to achieve full color (red, green and blue emitters). Etching of organic films and photoresist processing for lithography on organic films has proven to be technically very difficult and expensive. Therefore, instead of making a blanket film of one color, etching and making a blanket film of another color, it would be beneficial to make one blanket film and later locally change the properties of the film to emit different light colors. Thus, the need for etching would be removed.

Another approach is ink-jet printing local regions, but a problem associated with ink-jetting printing is that the dots printed do not have a uniform thickness.

Accordingly, what is desired, and has not heretofore been developed, is a method to modify the properties of a film after it has been formed, by introducing therein or removing impurities to modify the properties therefrom.

OBJECTS AND SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for manufacturing optoelectronic organic films having locally modified areas.

Another object of the present invention is to provide an organic film with various regions of modified optoelectronic properties.

Still another object and advantage of the invention is to form an organic film with modified properties by applying dopants in desired places.

A further object and advantage of the invention is the provision of a method for forming an organic film with local modified areas by adding impurities to or removing impurities from the film.

Even another object of the invention is to provide a method for locally modifying properties of an organic film without the need for photolithography and etching of the organic film.

A still further object and advantage of the invention is the provision of a method for manufacturing a locally modified organic film with the need for contacting the surface of said film with solvents.

Even an additional object of the invention is to provide a process of forming a locally modified organic film wherein dopant is added to the film in an annealing process.

Yet an additional object of the present invention is to provide a process for transferring a dopant from one layer to another layer.

A further object of this invention is the provision of a process for transferring a dopant from one layer to another layer in a desired pattern.

The methods of this invention involve modification of the properties of an organic film after it has been deposited by either adding new components into it from its top or bottom surface, or by causing components to leave the film from its top or bottom surface. In the examples of these methods, the emitting color of light-emitting diodes are modified based on doped polymers by locally introducing dopants causing different color emission into the film by local application of a solution containing the desired dopant to the film surface (by ink jet printing, screen printing, local droplet application, etc.). This overcomes difficulties encountered with the direct patterning of three separately formed

organic layers (each which uniformly coats an entire surface when formed) into regions for separate R, G, and B devices due to the sensitivities of the organic materials to chemicals typically used with conventional patterning technologies. Alternatively, dopants may be introduced in an organic film by diffusion from one layer into the film in local regions or by locally applying them directly into the organic film. Alternatively, dopants may be selectively removed from a film with solvents, etc.

Typically all of the active components are incorporated into the polymer when the polymer film is first formed, for example by spin coating it over a surface. In the present invention, the properties of the material are modified after a solid film has been formed by later introducing new species into the film from either its top or bottom surface, or removing impurities out through the top or bottom surface especially in a patterned arrangement. The method is especially attractive for the local modification of the photoluminescence and/or electroluminesence color of a thin film of the material, for example to create red, green, and blue light-emitting regions after a surface has been coated with a thin film of the material which is the same everywhere.

BRIEF DESCRIPTION OF THE DRAWINGS

Other important objects and features of the invention will be apparent from the following Detailed Description of the Invention taken in connection with the accompanying drawings in which:

FIGS. 1a and **1b** are diagrams of the application of dye on top of PVK film.

FIGS. 2a and **2b** are diagrams of dye on PVK film under UV illumination.

FIG. 3 is a plot of photoluminescence of materials used in **FIGS. 1-2**.

FIG. 4a is a diagram of a device and **FIG. 4b** is a plot of the electroluminsence spectra of PVK and C6.

FIGS. 5a and **5b** are diagrams of removal of local dye with acetone.

FIG. 6a is a diagram of a device and **FIGS. 6b** and **6c** photographs of the device of **FIG. 6a** under UV illumination.

FIG. 7 is a photograph under UV illumination of a device fabricated with an ink jet printer;

FIG. 8a is an experiment showing the effects of temperature on devices fabricated in accordance with the invention, and **FIG. 8b** is plot thereof.

FIG. 9 is a photograph under UV illumination of a device formed in accordance with the invention at increasing temperatures.

FIGS. 10a - 10c illustrate the steps in introducing film dopants from the top.

FIGS. 11a - 11c illustrate the steps in introducing dopants from the bottom.

FIGS. 12a -12c illustrates the steps for spatially modifying properties of polymer film.

FIGS. 13a - 13b illustrate the spectra of PVK and PVK with C6.

FIGS. 14a - 14c illustrate the steps in removing dopant from a polymer film into the underlying layer.

FIGS. 15a - 15c illustrate the steps in forming patterned addition of dopant from the top.

FIGS. 16a - 16c illustrate the steps in fabrication of patterned OLEDs.

FIGS. 17a - 17d illustrate the steps in fabrication of a passive matrix.

FIGS. 18a - 18c illustrate the steps in removal of dopant from polymer film in a pattern to the underlying layer.

FIGS. 19a - 19b illustrate the steps in removal of dopant from the top of a film.

FIGS. 20a - 20c illustrate the steps in the patterned removal of dopant from the top of a film.

FIGS. 21a - 21d illustrate the steps in fabrication of an active matrix OLED display.

DETAILED DESCRIPTION OF THE INVENTION

The goal of fabricating full color flat panel displays has the potential to be reached using organic light emitting diodes (OLEDs). The difficulty with using this technology is that the current deposition techniques, such as spin-coating and evaporation, deposit blanket films. The film can be used to make devices of a single color. To achieve individual emitters of different color next to each other, such as red, green, and blue, the deposited blanket film must be typically etched into a pattern, as might be done by photolithography followed by etching. Then, this process has to be repeated for multiple layers to achieve full color (red, green and blue emitters). Etching of organic films and photoresist processing for lithography on organic films has proven to be technically very difficult and expensive. Therefore, instead of making a blanket film of one color, etching and making a blanket film of another color, it would be beneficial to make one blanket film and later locally change the properties of the film to emit different light colors. Thus, the need for etching would be removed.

The present invention, in a broad, general sense, relates to the application of an organic film and thereafter modifying local characteristics thereof by adding or removing components, i.e. dopants, dies, etc., to or from the film to change the local characteristics of the film. Specifically, the invention relates to modifying the optoelectronic properties of an organic film by impurity or additional removal in a patterned fashion after application of the film. Even more specifically, the invention relates to modifying the emitting color of light-emitting diodes based on doped polymers by locally introducing dopants causing different color emission into an organic film by local application of solutions containing desired dopants to the film surface, i.e. by ink-jetting or screen printing. Alternatively, impurities contained within the film prior to application can be removing therefrom in desired patterns through various methods such as by the application of solvents.

One way for achieving this result is to locally dye a poly(9-vinylcabazole) (PVK a hole transporting polymer) spun-on film, with green, red and blue dyes. The dyes would dissolve in acetone or trichloroethylene (TCE), solvents that do not dissolve PVK, and could be patterned on top of the PVK film using an ink-jet printer. As shown in **FIGS. 1a and 1b**, the dopants diffuse into the film and the

solvent evaporates. Then metal cathodes could be patterned on top of the locally dyed regions, thus achieving full color integration.

To verify this technique, droplets of coumarin 6 (C6, a green dye) dissolved in TCE and Acetone were placed onto a spun-on 1000 angstrom thick PVK film using a pipette and the solvents were given time to evaporate. **FIG. 2a** shows a picture of these drops taken from above with a UV lamp shining on them to excite fluorescence of the organic film. Under UV, they appear to be a greenish yellow color. These droplets were also placed onto glass where no diffusion occurs and the C6.remains on the surface, and the solvents were allowed to evaporate, as shown in **FIG. 2b**. Under UV lamp they appear to be a reddish color. This indicates that when the drops are placed onto a PVK film there is some interaction with the PVK, because when the PVK is present the dyed areas appear greenish-yellow, and when the PVK is not present the dye appears red. The interaction is the diffusion of the dye into PVK.

In order to state the above observations in a more quantitative way, a photoluminescence spectra was taken. **FIG. 3** shows the PL spectra of a pure PVK film (peak at 410 nm), a PVK film locally dyed with C6 (peak at 490 nm), a blend film, where the PVK was dyed in solution with C6 (peak a 490 nm), and the dye on glass (peak at 580 nm). This provides evidence that not only does the dye interact with the PVK, but it interacts in such a way that the PL spectra is nearly identical to that of a blend film, which is known to be able to be made into a device. Therefore, the next step was to attempt to make a device using this locally dyeing procedure.

FIG. 4a shows the device structure, and **FIG. 4b** shows the electro-luminescence (EL) spectrum of the device and the EL of a blend device made by dissolving PVK and C6 in chloroform, spinning the film, and evaporating contacts. To make the locally dyed device, PVK dissolved in chloroform was spun onto glass coated with indium tin oxide (ITO, a transparent conductor). Next, a drop of C6 dissolved in acetone was dropped onto the surface, the sample was then spun again. Finally, a metal contact was evaporated on top of the dyed area. The EL spectra of the locally dyed device is seen to have the same 490 nm peak as the blend device Therefore, this shows that the dye not only interacts

with the PVK, but it interacts in such a way that a device can be made which has a similar EL spectra to blend device.

In order to further investigate this locally dyeing phenomenon, an experiment was set up to see if dye could be washed out of a blend film, which had been dyed in solution. **FIG. 5a** and **5b** shows a schematic of the experiment. First, PVK and C6 were dissolved in chloroform. Next, they were spun-on to an ITO coated glass substrate, forming a 1000 angstrom film. When this film was observed under a UV lamp, it appeared green. Next, a drop of acetone was dropped onto the surface. When a UV lamp was shone onto the sample, it was observed that where the drop of acetone had been, the sample was blue, and where it had not been, the sample was green. This indicates that the dye could be washed out of a blend film, which created a local area without dye. Therefore, two different color LEDs could be made on a substrate which had been locally washed.

FIG. 6a shows a schematic of the device made on the washed film. The film was prepared as mentioned above, and then metal cathodes were evaporated in the washed areas and in the non-washed areas. These cathodes were thermally evaporated and were patterned by a shadow mask. **FIGS. 6b** and **6c** are pictures of the devices, from below, emitting light. **FIG. 6b** shows a device emitting green (appears light blue because of camera used) and **FIG. 6c** shows an emitting blue. The green device is emitting green because the metal cathode was evaporated on top of the dyed film, and the blue device is emitting blue, because the metal cathode was evaporated on top of the washed film.

Thus, devices can be made by locally dyeing a PVK film, or by locally washing a dyed PVK film. Therefore, the next step is to pattern the dye using an ink-jet printer. **FIG. 7** shows a picture of a piece of glass coated with ITO, onto this glass was spun a 1000 angstrom thick film of PVK. Then an Epson Stylus Color 400 ink-jet printer was used to pattern C6 dissolved in acetone on top of the film. The sample was then illuminated under UV. This shows that the dyes can be patterned by an ink-jet printer with a spot diameter of ~500 μm. The next step is to try to determine the ultimate resolution of this technique.

An experiment was done to determine if the diameter of the printed spots could be influenced by temperature. **FIG. 8a** shows the experimental set-up, a 1000 angstrom film of PVK was spun onto a piece of glass coated with ITO. The sample was then placed onto a hot plate. Droplets of equal volume of C6 dissolved in acetone and equal volumes of C6 dissolved in TCE were dropped on to the PVK film at different temperatures. It was observed that at higher temperatures the spots did not spread as far and therefore had smaller diameters. This is shown in the plot of **FIG. 8b.** This could potentially make the spot size ~0.6 times smaller. However, this data does not reveal the difference observed in using TCE and acetone.

FIG. 9 shows a picture of the same spots dropped onto the PVK film at increasing temperatures lit up by a UV lamp. What can be seen is that there are, at higher temperatures in the TCE drops, bright yellow spots which are ~ 1/3 of the outer spot, and have a more intense luminescence. This may be because, as the solvent dries the C6 tends to stay in the solution and what is left at the end is a highly concentrated small diameter spot. When this spot profile is checked using a surface profilometer it is seen that the dye is actually sitting on the surface. Therefore, in order to take advantage of this small diameter, the substrate would have to be heated further, to allow the dye to thermally diffuse into the film.

In conclusion, PVK can be locally dyed by dissolving dye in acetone or TCE and dropping it on to the surface. Also, this dyed area can be made into a device. A blend film of PVK and C6 can have the C6 locally washed out of it using acetone, and a device can be made using this technique. At the present time ink-jet printed dyed lines can be made with widths of ~500 μm. This width can be further reduced by printing with TCE onto a heated substrate to obtain a spot 1/10 of the diameter of a spot made at room temperature. This substrate would have to then be heated again to thermally diffuse the dye into the film.

FIGS. 10a-10c illustrate the basic method for introducing film dopants from the top in the fabrication of red, green and blue OLED devices on a common substrate. As shown in **FIG. 10a**, a uniform film of polymer **10** without the desired dopant is formed on substrate **11**. The polymer film **10** may contain other

dopants. In **FIG. 10b**, dopant **12** is placed on the surface of the polymer film **10** by evaporation, spin coating, or other method. In **FIG. 10c** annealing or other process caused the dopant **12** to enter the film **10** by diffusion or by other methods. The solvents used in spin coating the dopant **12** on the surface may cause dopant **12** to enter polymer **10** and be deposited into it without need for the steps described in **FIG. 10c**. In this case there is never a solid dopant layer on the surface.

FIGS. 11a-11c show the introduction of dopants into a film from the bottom thereof. In **FIG. 11a**, a substrate **13** has a coating **14** put down thereon. The coating 14 may contain the desired dopant or, the dopant may be applied in the manner described in **FIGS. 10a-10c** (i.e. may be polyanaline or similar hole transport layer in OLED). As shown in **FIG. 11b**, the polymer film **15** is deposited onto the coating **14**. In **FIG. 11c**, annealing causes dopant to partially migrate from layer **14** into polymer film **15**. It should be noted that the solvents used in spin coating the top polymer may "leach" dopant out of the underlying layer without the need for the thermal cycling described in **FIG. 11c**.

FIGS. 12a-12c show the steps of a method for spatially modifying the properties of the polymer film. **FIG. 12a** illustrates the deposition of a polymer **16** onto a substrate **17** in the same manner as discussed in connection with **FIG. 10a**. **FIG. 12b** shows the creation of local regions of different dopants, **18** and **19** on the polymer surface 16 by local deposition methods such as evaporation through different shadow masks, deposition by screen printing using different screens, or by ink jet printing, or other printing processes using different patterns for each dopant. **FIG. 12c** illustrates the heat treatment of the structures of **FIG. 12b** by annealing, for example, to cause the dopant **18** and **19** to migrate into the polymer **16**. As discussed in connection with **FIGS. 10a-10c**, solvents used in screen printing or in ink jet printing may carry dopants directly into the polymer so that the heat treatment step of **FIG. 12c** may not be required.

This has been demonstrated using dyes C6 (green), C47 (blue), and nile red (green) in acetone solution separately applied to individual regions of a single PVK film, where acetone solution is locally applied by an eyedropper or similar device. Acetone does not cause removal of PVK film, but after evaporation of

acetone in a few seconds the fluorescence color of the film under UV excitation has changed.

As illustrated in **FIGS. 13a-13b**, both the photoluminescence (**FIG. 13a**) and electroluminesence (**FIG. 13b**) show the shift between pure PVK film and doped PVK.

The dopant need not be pure dopant, but may be co-deposited with another material. Subsequent process (or the very deposition process itself) can then cause dopant to move into underlying layer. Other material may be removed or remove itself (evaporate), or stay behind as separate layer and be part of final structure doped or undoped.

The spatial variations of **FIGS. 12a-12c**, may be applied to the method described in connection with **FIGS. 11a-11c** so that patterns of dopant may be introduced into underlying material before top polymer film is deposited.

FIGS. 14a-14c illustrate the steps in the removal of dopant from polymer film into an underlying layer. In **FIG. 14a,** substrate **19** has a bottom absorber film layer **20** deposited thereon. The absorber layer has a low chemical potential for the desired dopant. In **FIG. 14b**, the doped polymer **21** is deposited onto the absorber layer **20**. In **FIG. 14c**, annealing or another cycle which causes the dopant to move is applied. In lieu of the heating treating, a solvent may be applied which infiltrates (from the top) both the polymer layer **21** and the bottom layer **20** to enable the dopant in the top polymer layer to migrate into the bottom layer **20**.

FIGS. 15a-15c shown the patterned addition of dopant from the top with an impermeable barrier. In **FIG. 15a**, the undoped polymer **23** is deposited on substrate **22**. In **FIG. 15b** , a patterned layer impermeable by the dopant **24, 25, 26** is formed on the top of the polymer **23**. In **FIG. 15c** dopant **27** in ambient is heat treated by annealing. Alternatively, the structure of **FIG. 15b** may be placed into a solvent containing the dopant

FIGS. 16a-16c illustrate the application of the method described in **FIG. 12** to the formation of patterned OLEDs of different colors. As shown in **FIG. 16a**, undoped polymer **30** is deposited everywhere onto ITO layer **29** on glass substrate **28**. The ITO may be patterned. Local red (**31**), green (**32**) and blue (**33**) regions are formed by locally doping the polymer **30**. These red, green and blue

regions may be formed by ink jet printing three different solutions in different regions. Heat treating may then be applied. In **FIG. 16c**, top contacts **34**, **35**, **36** are formed on the red, green, and blue regions by standard methods such as by evaporation through a shadow mask. In making OLED's applying color dopant by using localized solvent may change any dopants which were in film from original spin coating (e.g. PBD for electron transport). So, some of this dopant may need to be put in with the color dopant solution.

FIGS. 17a-17d illustrate the application of the method described in **FIG. 12** to form a passive matrix color OLED display. In **FIG. 17a**, ITO lines **37** are formed in one direction on glass substrate **38**. In **FIG. 17b**, a uniform polymer film **39** is applied over the ITO lines. In **FIG. 17c**, red, green, blue doped polymer **40** is formed on the ITO lines in the polymer film as by the steps described in **FIG. 16b**. **FIG. 17d** cathode lines **41** as top contacts perpendicular to the bottom contact lines **37**. Doping need only be in the region of the intersection of the top and bottom contact lines.

FIGS. 18a-18c illustrate the removal of dopant from polymer film in a pattern to the underlying layer. In **FIG. 18a**, the absorber film **43** is deposited onto substrate **42**. In **FIG. 18b**, absorber film **43** is patterned or coated with a patterned impervious layer **44**. Doped polymer **45** is added onto the layer **44**. **FIG. 18c** shows the effect of annealing or other treatment of the structure of **FIG. 18b** in causing the doping to move into the underlying layer **43**, where it is not impeded by the impervious barrier. The movement of the dopant may be accomplished through the use of a solvent as discussed in connection with **FIG. 14c**.

FIGS. 19a-19b shows the removal of dopant from the top of an unpatterned film. In **FIG. 19a**, doped film **47** is deposited onto a substrate **46** as by spin coating with dopant in solution. **FIG. 19b** illustrates the treatment of the structure of **FIG. 19a** by annealing in certain ambients or washing with solvent to the cause the reduction of dopant in layer **47**. Washing by applying the drop may not remove the dopant from the film, but cause it to move to the edge of the drop location, leaving little dopant in the center of the drop.

FIGS. 20a-20c illustrate the patterned removal of dopant from the top of the film. In **FIG. 20a**, doped polymer film **49** is deposited onto substrate **48**. In

FIG. 20b patterned impermeable layer **50** is applied over the doped polymer layer **49**. In **FIG. 20c**, annealing the structure of **FIG. 20b** causes dopant to evaporate in areas without barrier **50**. This evaporation may also be accomplished by washing with solvent to remove dopant in the areas without barrier **50**, or treating with a solvent vapor.

FIGS. 21a-21d show the formation of an active matrix OLED display. In **FIG. 21a**, glass substrate **51** has patterned insulator **52** and electrodes **53** formed thereon. The electrodes are connect to transistors (not shown) in the pixels. In **FIG. 21b**, undoped organic layer **54** is deposited everywhere on the structure of **FIG. 21a**. In **FIG. 21c**, locally applied red (**55**), green (**56**) and blue (**57**) dopant is applied as by ink jet printing. As shown in **FIG. 21d**, top electrode **58** is applied without a pattern. Top electrode **58** may be, for example Al:Li or Mg:Ag cathode.

The methods described in this invention may be applied to any organic film, not just polymer based. Solvent methods may cause problems with small organic molecule based films, however, dopants could be deposited by diffusion by thermal treatment by other localized methods such as evaporation through a mask, etc.

It should be further understood that "undoped" means not doped with the dopant being added or removed. Other dopants may be present.

Having thus described the invention in detail, it is to be understood that the foregoing description is not intended to limit the spirit and scope thereof. What is desired to be protected by Letters Patent is set forth in the appended claims.

CLAIMS

What is claimed is:

1. A method for manufacturing an organic film for organic light emitting diodes, the organic film having areas with modified properties, comprising the steps of:

providing a substrate;

coating an organic material thereon to form an organic film; and

applying a dopant to areas of the film to modifiy the properties of the film in desired areas.

2. The method of claim 1 wherein the dopant is applied by application of liquid droplets.

3. The method of claim 2 wherein the liquid droplets are applied by ink-jet printing.

4. The method of claim 2 where the substrate is heated to reduce the size of the modified area.

5. The method of claim 1 wherein the dopant is applied by screen printing.

6. The method of claim 1 wherein the dopant modifies the light emitting properties of the organic film.

7. The method of claim 6 wherein the dopant comprises red, green or blue dyes.

8. The method of claim 7 wherein the dopant includes coumarin and nile red.

9. A method of manufacturing a locally modified organic film comprising the steps of:

providing a substrate;

applying an organic coating having a dopant; and

removing the dopant from areas of the coating.

10. The method of claim 9 wherein dopant is removed from the coating by a solvent applied to a surface of the coating.

11. The method of claim 9 wherein the dopant is removed from the coating by annealing which caused the dopant to migrate from the coating.

12. The method of claim 10 wherein a mask is patterned on the coating prior to applying the solvent to remove the dopant in a pattern.

13. The method of claim 11 wherein a mask is patterned on the coating prior to annealing to remove the dopant in a pattern.

14. The method of claim 10 wherein the solvent is applied in a pattern onto the coating to remove the dopant in a pattern.

15. A method of manufacturing a locally modified organic film comprising:

providing a first layer having a dopant;

providing a second layer on the first layer; and

transferring the dopant from the first layer to the second organic layer.

16. The method of claim 15 wherein the dopant is transferred in selected areas from the first layer to the second organic layer.

17. The method of claim 16 wherein masking means is provided on the first layer prior to providing the second organic layer, and the dopant is transferred from the first layer to the organic second layer in areas not masked.

18. The method of claim 16 wherein the first layer with the dopant is patterned on a substrate, and the dopant is transferred to second in the pattern of the first layer.

19. A method of manufacturing a locally modified organic film comprising of:

providing a first layer of material;

applying a dopant in a pattern to the first layer;

providing a second layer comprising an organic material; and

transferring the dopant from the first layer to the second layer in the pattern.

20. The method of claim 19 wherein the dopant is applied by application of liquid droplets.

21. The method of claim 20 wherein the liquid droplets are applied by ink-jet printing.

22. The method of claim 20 where the substrate is heated to reduce the size of the modified area.

23. The method of claim 19 wherein the dopant is applied by screen printing.

24. The method of claim 19 wherein the dopant modifies the light emitting properties of the organic film.

25. The method of claim 24 wherein the dopant comprises red, green or blue dyes.

26. The method of claim 25 wherein the dopant includes coumarin and nile red.

27. The method of claim 19 wherein the dopant is transferred by annealing.

28. A method of locally modifying properties of an organic film for an OLED comprising the steps of:

providing a substrate;

applying an organic coating thereon;

depositing a dopant or material containing a dopant thereon; and

causing the dopant to migrate into the organic coating.

29. The method of claim 28 wherein the dopant is applied to the organic coating in a pattern, and the dopant forms the pattern in the organic layer after the dopant migrates thereinto.

30. The method of claim 29 wherein the dopant is applied by liquid droplet application.

31. The method of claim 29 wherein liquid droplets are applied by ink jet printing.

32. The method of claim 29 wherein the dopant is applied by patterning dry powder onto the organic coating.

33. The method of claim 29 wherein the dopant is applied by placing a patterned thin foil containing the dopant in close contact with the organic coating.

34. The method of claim 29 wherein the dopant is caused to migrate into the organic layer by the application of heat.

35. The method of claim 30 where the substrate is heated to reduce the size of the modified area.

36. A method of manufacturing a locally modified organic film comprising the steps of:

providing an organic film;

covering the organic layer with a patterned barrier;

applying a dopant or material containing a dopant over the organic layer and the barrier; and

causing the dopant to migrate into the organic film in areas exposed through the barrier.

FIG. 1A

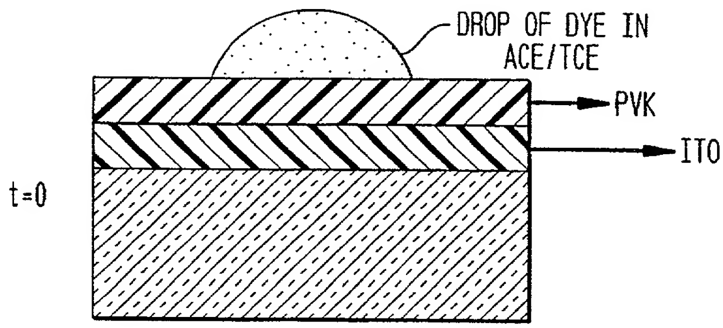


FIG. 1B

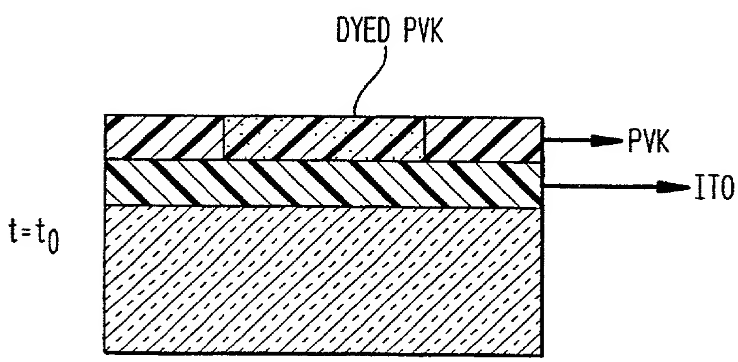


FIG. 2A

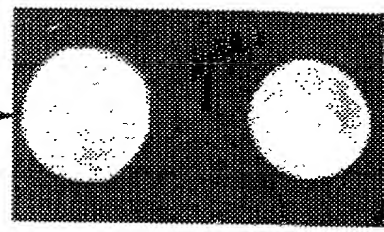
C6 IN ACETONE

C6 IN TCE

FIG. 2B

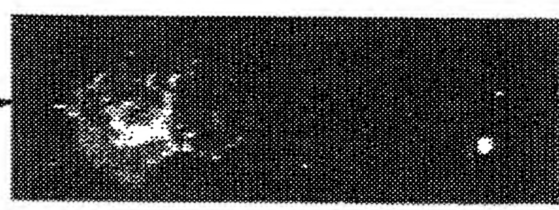
C6 IN ACETONE

C6 IN TCE

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FIG. 3

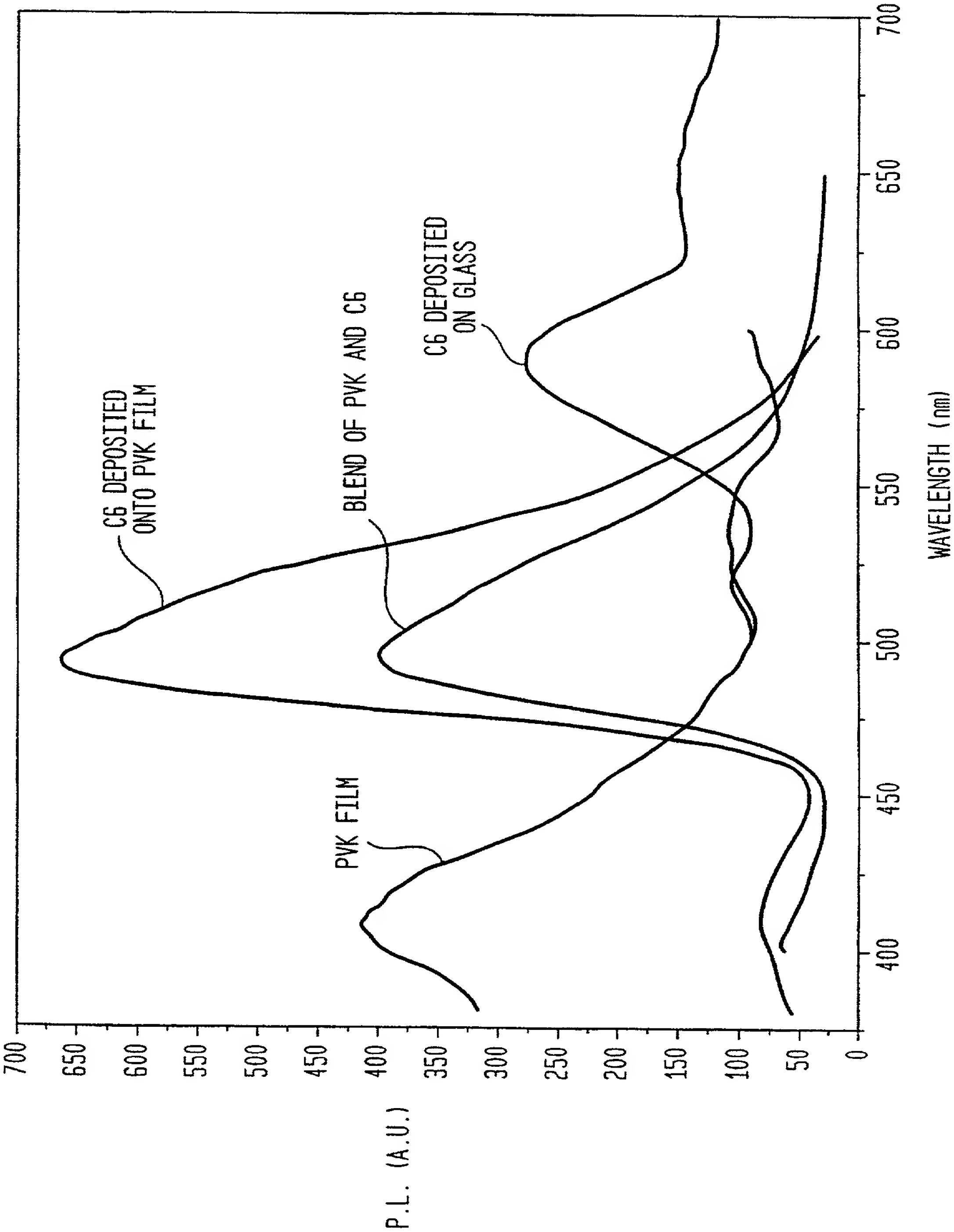

FIG. 4A

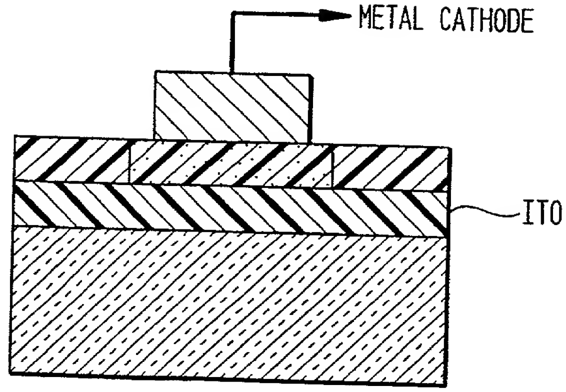
METAL CATHODE
ITO

FIG. 4B

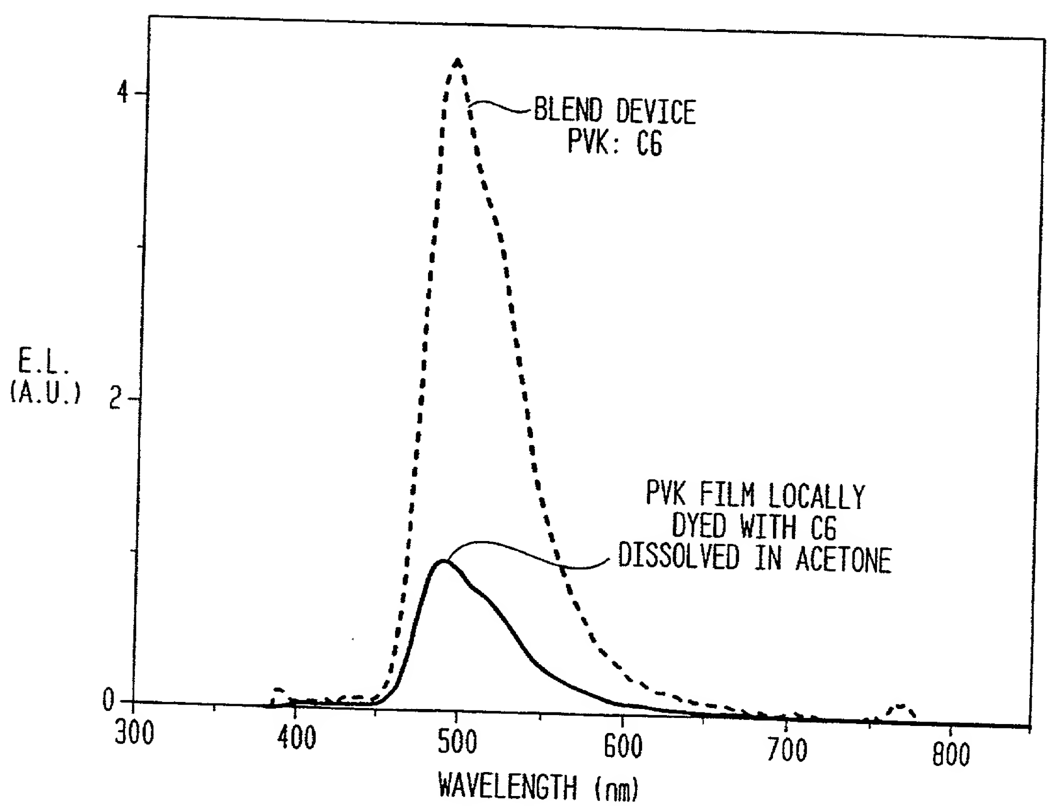
BLEND DEVICE
PVK: C6
PVK FILM LOCALLY
DYED WITH C6
DISSOLVED IN ACETONE
E.L.
(A.U.)
4
2
0
300
400
500
600
700
800
WAVELENGTH (nm)

FIG. 5A

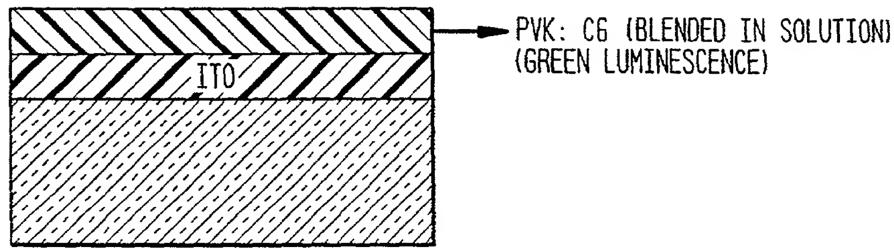
ITO
PVK: C6 (BLENDED IN SOLUTION)
(GREEN LUMINESCENCE)

FIG. 5B

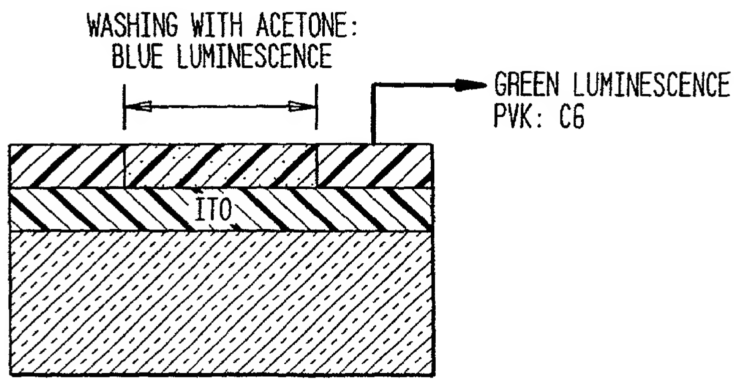
WASHING WITH ACETONE:
BLUE LUMINESCENCE
GREEN LUMINESCENCE
PVK: C6
ITO

FIG. 6A

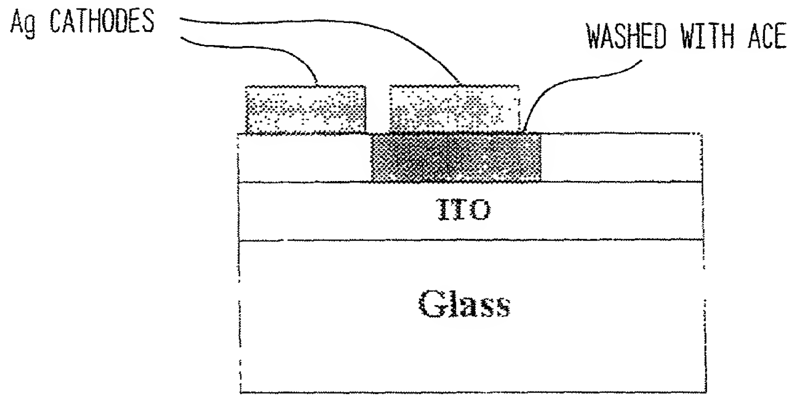

FIG. 6B

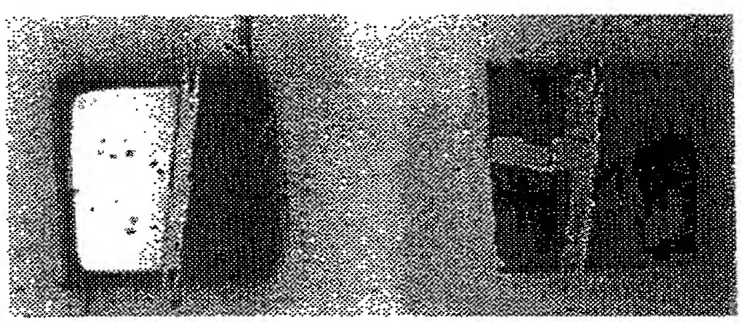

FIG. 6C

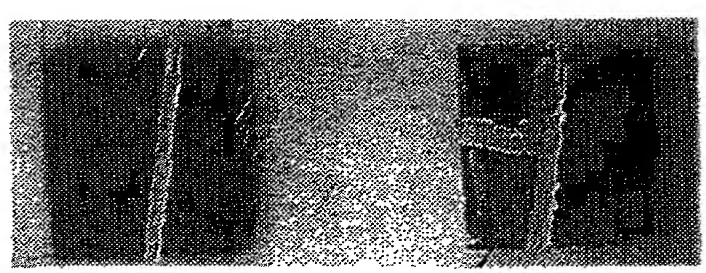

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FIG. 7

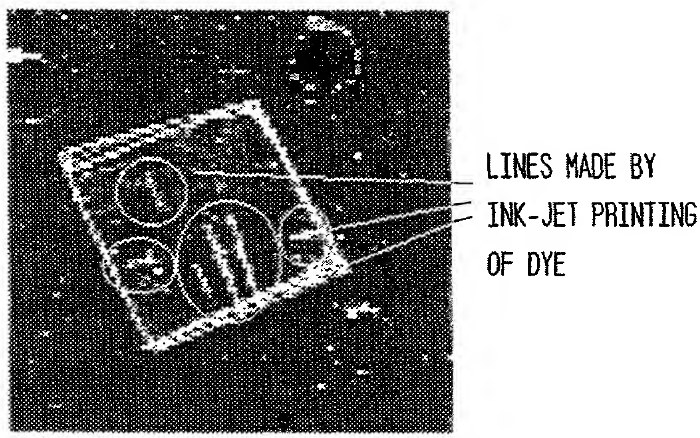

FIG. 8A

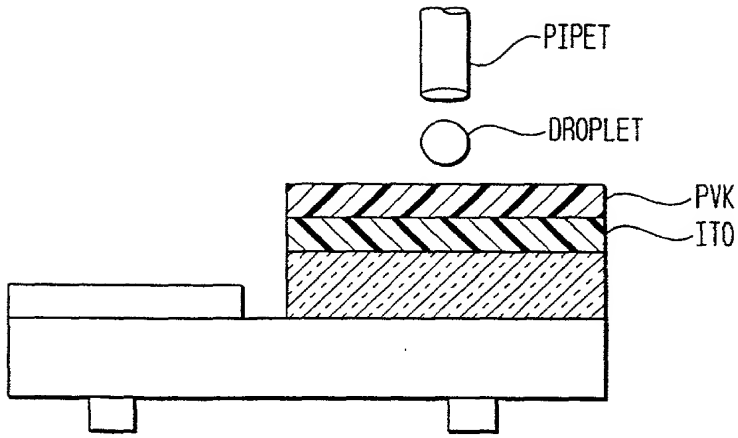
PIPET
DROPLET
PVK
ITO

FIG. 8B

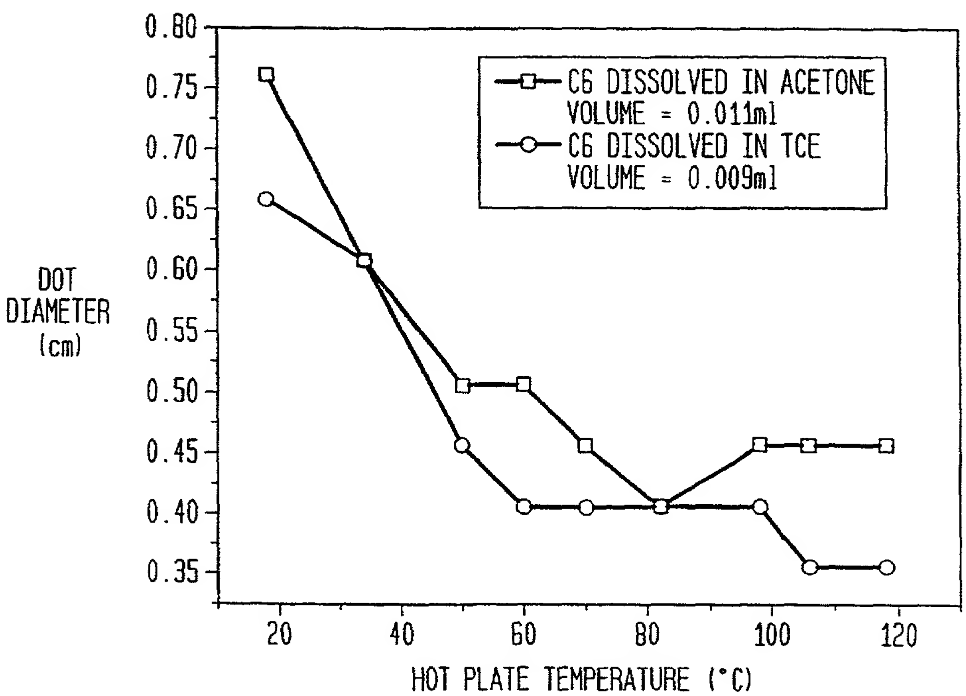
DOT DIAMETER (cm)
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
C6 DISSOLVED IN ACETONE VOLUME = 0.011ml
C6 DISSOLVED IN TCE VOLUME = 0.009ml
20
40
60
80
100
120
HOT PLATE TEMPERATURE (°C)

FIG. 9

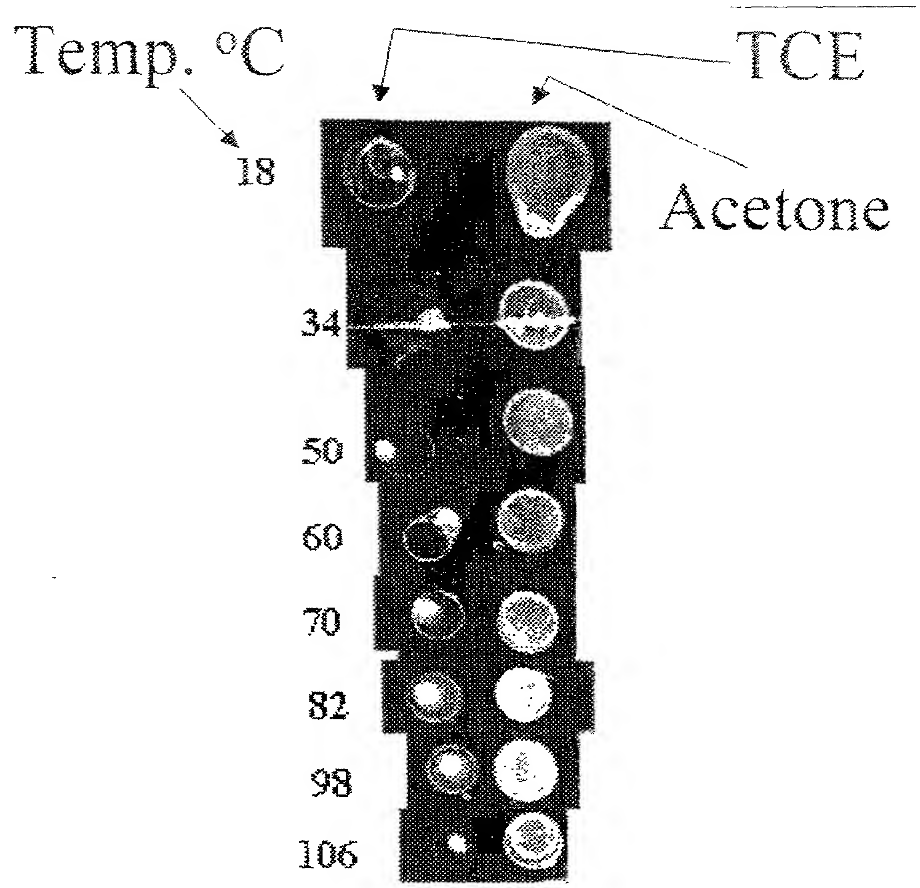

FIG. 10A

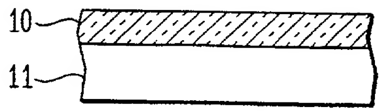

FIG. 10B

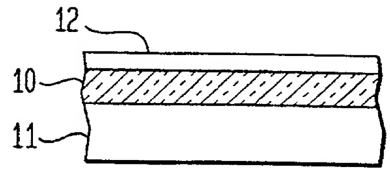

FIG. 10C

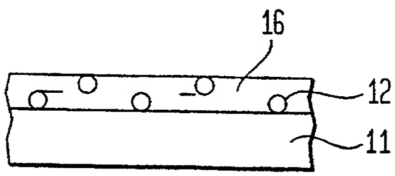

FIG. 11A

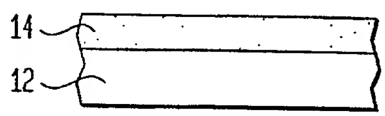

FIG. 11B

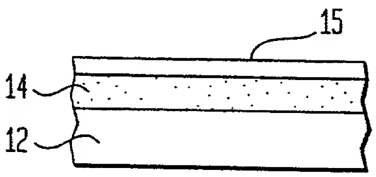

FIG. 11C

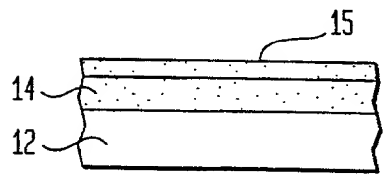

FIG. 12A

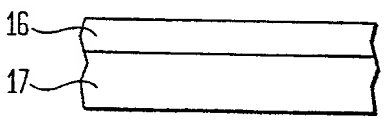

FIG. 12B

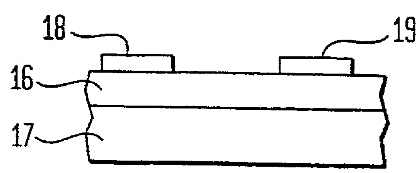

FIG. 12C

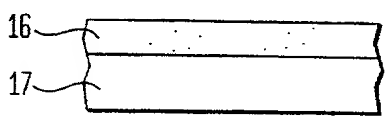

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FIG. 13A

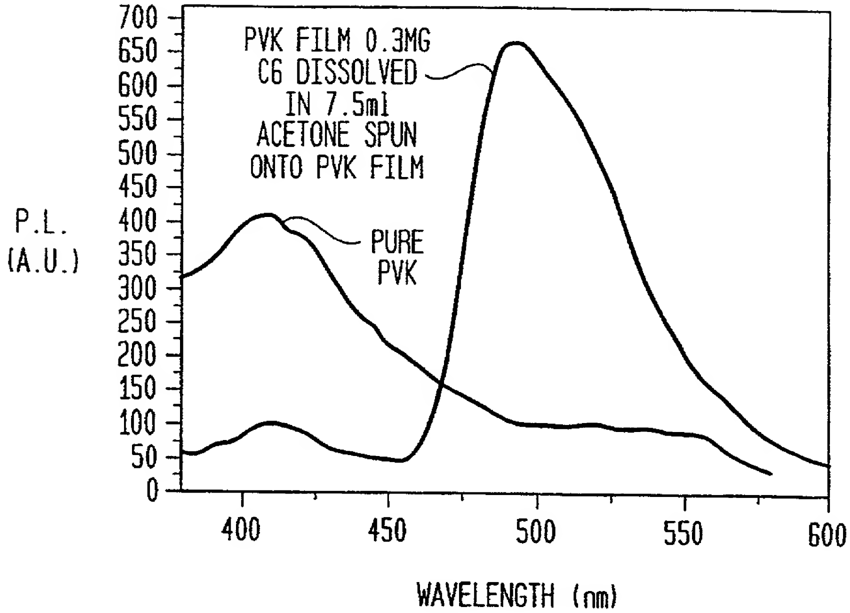


FIG. 13B

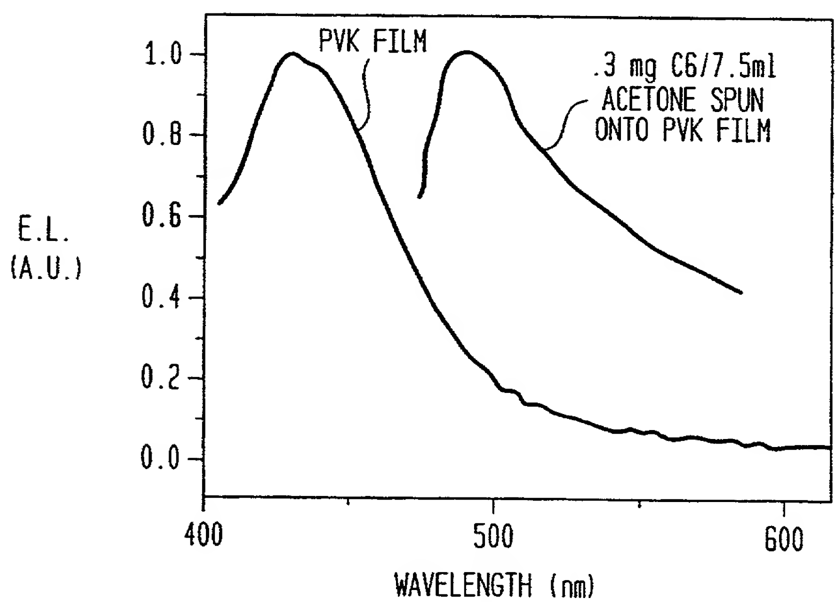


FIG. 14A

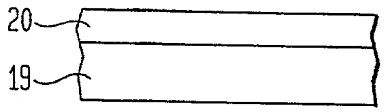


FIG. 14B

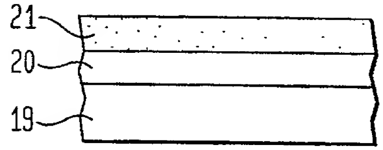


FIG. 14C

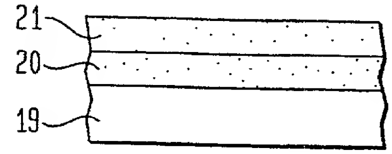


FIG. 15A

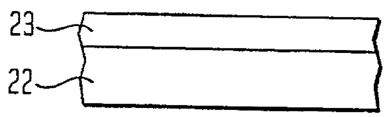


FIG. 15B

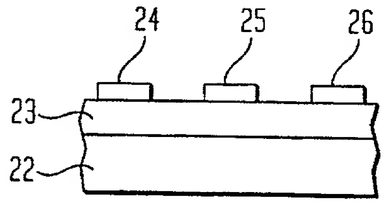


FIG. 15C

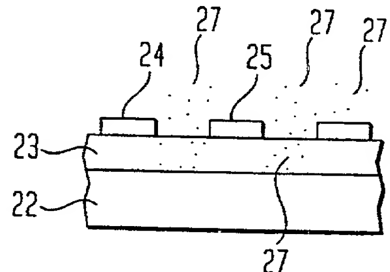


FIG. 16A

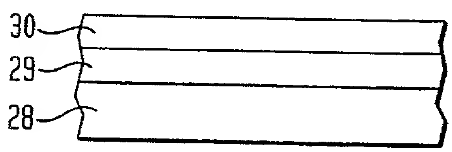


FIG. 16B

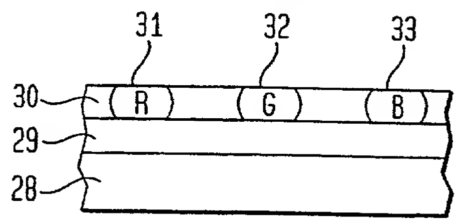


FIG. 16C

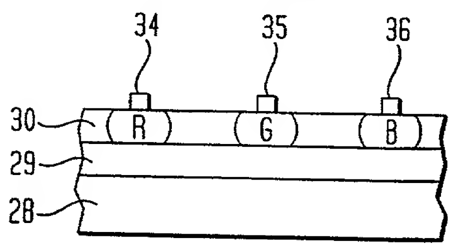


FIG. 17A

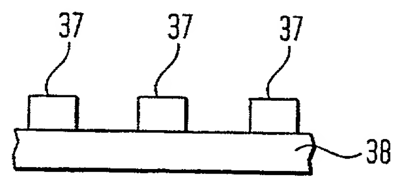


FIG. 17B

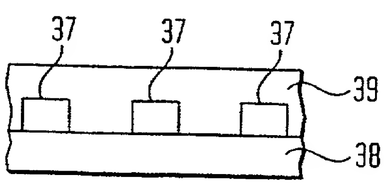


FIG. 17C

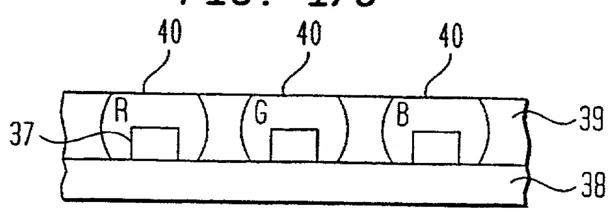
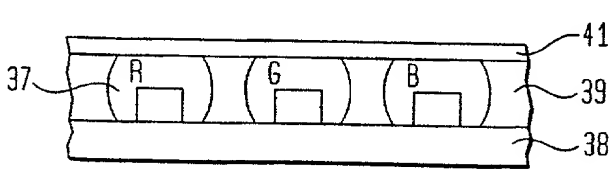


FIG. 17D



SUBSTITUTE SHEET (RULE 26)

FIG. 18A

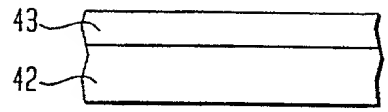


FIG. 18B

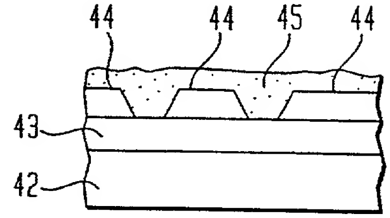


FIG. 18C

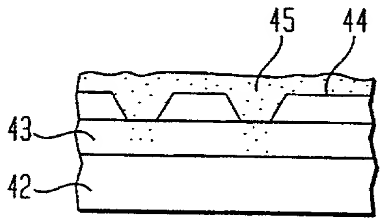


FIG. 19A

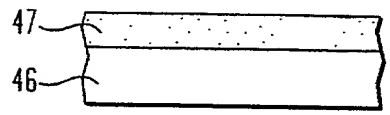


FIG. 19B

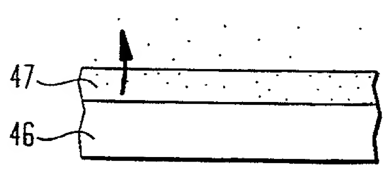


FIG. 20A

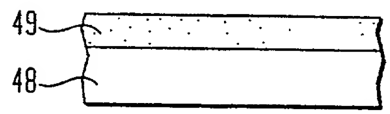


FIG. 20B

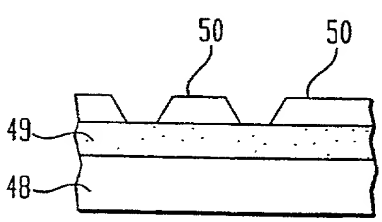


FIG. 20C

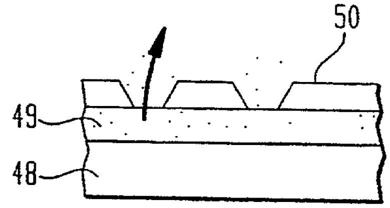


FIG. 21A

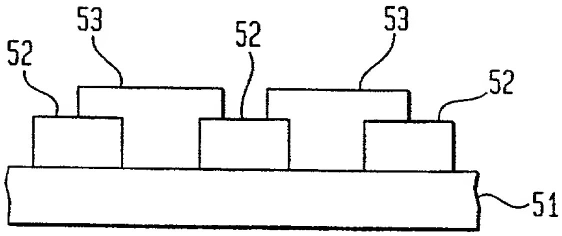


FIG. 21B

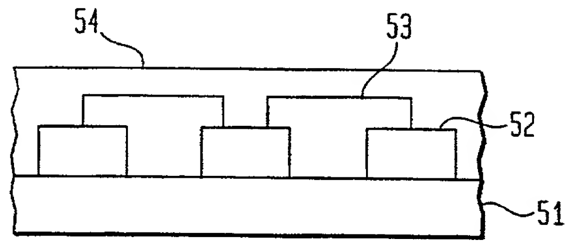


FIG. 21C

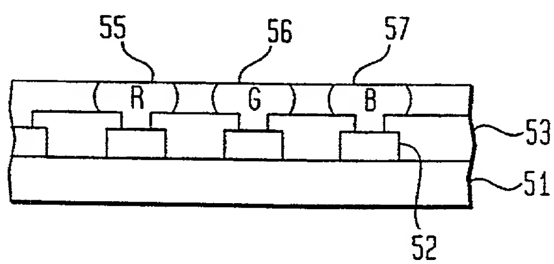
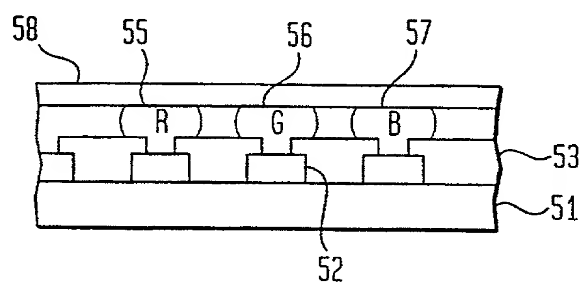


FIG. 21D



Docket No.
7616/21

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Modification of Polymer Optoelectronic Properties After Film Transition by Impurity Addition or Removal

the specification of which
(check one)

☐ is attached hereto.

☒ was filed on April 12, 1999 as United States Application No. or PCT International Application Number PCT/US99/07970

and was amended on ______________________

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

			Priority Not Claimed
(Number)	(Country)	(Day/Month/Year Filed)	☐
(Number)	(Country)	(Day/Month/Year Filed)	☐
(Number)	(Country)	(Day/Month/Year Filed)	☐

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

60/081,492	04/13/98
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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Registration No. 33,884

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Full name of sole or first inventor **James C. Sturm**	
Sole or first inventor's signature James C Sturm	Date 1/26/01
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Citizenship **USA**	
Post Office Address **278 Riverside Drive, Princeton, NJ 08540**	

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Second Inventor's signature	Date
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Citizenship **USA**	
Post Office Address **186 Malliuson Street, Allendale, NJ 07401**	

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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Third inventor's signature	Date 1/21/01
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Citizenship **Germany**	
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Full name of fourth inventor, if any	
Fourth inventor's signature	Date
Residence	
Citizenship	
Post Office Address	

Full name of fifth inventor, if any	
Fifth inventor's signature	Date
Residence	
Citizenship	
Post Office Address	

Full name of sixth inventor, if any	
Sixth inventor's signature	Date
Residence	
Citizenship	
Post Office Address	

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) AND 1.27 (d)) - NONPROFIT ORGANIZATION

Docket No. 7616/21

Serial No.	Filing Date	Patent No.	Issue Date

Applicant/ Patentee: **Sturm, et al.**

Invention: **Modification of Polymer Optoelectronic Properties After Film Transition by Impurity Addition or Removal**

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION: **The Trustees of Princeton University**

ADDRESS OF ORGANIZATION: **Princeton University**
P.O. Box 36
Princeton, NJ 08544-0036

TYPE OF NONPROFIT ORGANIZATION:

- ☒ University or other Institute of Higher Education
- ☐ Tax Exempt under Internal Revenue Service Code (26 U.S.C. 501(a) and 501(c)(3))
- ☐ Nonprofit Scientific or Educational under Statute of State of The United States of America
  Name of State: Citation of Statute:
- ☐ Would Qualify as Tax Exempt under Internal Revenue Service Code (26 U.S.C. 501(a) and 501(c)(3)) if Located in The United States of America
- ☐ Would Qualify as Nonprofit Scientific or Educational under Statute of State of The United States of America if Located in The United States of America
  Name of State: Citation of Statute:

I hereby declare that the above-identified nonprofit organization qualifies as a nonprofit organization as defined in 37 C.F.R. 1.9(e) for purposes of paying reduced fees to the United States Patent and Trademark Office regarding the invention described in:

- ☒ the specification to be filed herewith.
- ☐ the application identified above.
- ☐ the patent identified above.

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention.

If the rights held by the above-identified nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed on the next page and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

☒ no such person, concern or organization exists.
☐ each such person, concern or organization is listed below.

FULL NAME ____________________
ADDRESS ____________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME ____________________
ADDRESS ____________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME ____________________
ADDRESS ____________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME ____________________
ADDRESS ____________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING: **Allen J. Sinisgalli**
TITLE IN ORGANIZATION: **Associate Provost**
ADDRESS OF PERSON SIGNING: **Princeton University**
P.O. Box 36
Princeton, NJ 08544-0036

SIGNATURE: Allen J. Sinisgalli DATE: 9/22/00